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(54) NOVEL STARCH COMPOSITION AND PROCESS FOR PRODUCTION OF PAPER

(71) We, NALCO CHEMICAL COMPANY, a Corporation organized under the laws of the State of Delaware, United States of America, of 180 North Michigan Avenue, Chicago, State of Illinois, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a novel starch composition and to a process for manufacturing paper using said starch composition. It is particularly concerned with the manufacture of paper having improved dry strength and other improved properties.

The present invention provides a starch-polymeric polyamine composition comprising 60—98% by weight of starch, and 2—40% by weight of a polymeric polyamide having a molecular weight of at least 500, said starch-polymeric polyamide having been prepared by cooking an aqueous suspension of said starch with said polymeric polyamine at a temperature of 140—250° F. for ¼—10 hours, said polyamine being formed by reaction of an alkylene dihalide and an amine having the following structural formula:

$$H_2N(-R-\underset{}{\overset{H}{\overset{|}{N}}}-)_xH$$

where R is an alkylene radical selected from

$$-CH_2CH_2-,\ -CH_2CH_2CH_2-,\ \text{and}$$

$$-CH_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-,$$

and x is an integer of 0—5.

The present invention also provides a process for the production of paper having improved strength and other improved properties which comprises the sequential steps of forming an aqueous cellulosic fiber suspension, adding to said suspension as a single product at a point prior to its formation into a sheet, a polymeric polyamide starch composition, said starch composition having been prepared by reacting a 60—98% by weight aqueous suspension of starch with 2—40% by weight of a polymeric polyamide having a molecular weight of at least 500 at a temperature of 140—250° F. for ¼—10 hours, said polyamine being formed by reaction of an alkylene dihalide and an amine having the following structural formula:

$$H_2N(-R-\underset{}{\overset{H}{\overset{|}{N}}}-)_xH$$

where R is an alkylene radical selected from

$$-CH_2CH_2-,\ -CH_2CH_2CH_2-,\ \text{and}$$

$$CH_2\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-,$$

and x is an integer of 0—5; and then forming said aqueous cellulosic fiber suspension containing said modified starch into a sheet.

Starches of different types have been used in the production of paper for many years to achieve varying aims such as to increase sheet strength. Indicative of this wide-spread usage are the various uses of starch described in the article by M. L. Cushing and K. R. Schuman, "Fiber Attraction and Interfiber Bonding—The Role of Polysaccharide Additives," which appears in the December, 1959 issue of TAPPI.

One of the chief difficulties in using starch as a wet end additive for improving various papers is that it is difficult to adequately retain the starch on the sheet. In most instances the majority of starch added is lost in the

papermaking process. Many attempts have been made to improve retention of starch by cellulosic fibers.

In some instances efforts have been made to thermally modify starch. In other instances starch has been treated with chemicals in attempts to render it more susceptible to being retained by fibers. While both of these approaches have met with some measure of success in improving the retention characteristics of starches, nevertheless a high percentage of starch is lost through non-adherence to the paper fibers.

It would be advantageous to the art of papermaking if it were possible to provide a simple method for improving the ability of starch to be retained by cellulosic fibers. Also of interest would be a paper manufacturing process which in a series of operation steps, would render the common starches more receptive to cellulosic fibers by prior reaction of the starch materials with relatively inexpensive organic chemicals.

By improving the receptivity of cellulosic fibers to common starches reacted with organic chemicals, it should be possible to produce paper having a greater amount of starch contained therein. This will afford a finished sheet having superior dry strength and many other improved characteristics which flow from the incorporating therewith of bonded, well dispersed starches.

Based on the above, it is therefore an object of the invention to provide an improved process for the manufacture of paper.

An object is to furnish a method for simply reacting starch to produce a starch product of extreme value to the papermaking industry. Other objects will appear hereafter.

Another object is to provide a method whereby starch may be inexpensively and simply reacted just prior to introduction into the pulp stream so that it is highly receptive to cellulosic fibers.

In accordance with the invention, it has been found that an improved paper product may be provided by treating a papermaking stock prior to its formation into a sheet with a starch-polymeric polyamine composition. More particularly, it has been discovered that paper may be improved by treating an aqueous suspension of pulp with the just-mentioned starch-polymeric polyamine composition which has been prepared by reacting an aqueous suspension of starch with 2—40% by weight based on the weight of starch and polyamine of a specialized polymeric polyamine. This polyamine is formed by reaction of an alkylene dihalide and an amine having the following structural formula:

$$H_2N\left(-R-\overset{\displaystyle H}{\overset{|}{N}}-\right)_x H$$

where R is an alkylene radical selected from

$$-CH_2CH_2-,\quad -CH_2CH_2CH_2-,\ \text{and}\quad -CH_2\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}-,$$

and x is an integer of 0—5. R, when present, is preferably an ethylene radical. Preferred reactants are ammonia, ethylene diamine, diethylene triamine, tetraethylene pentamine and triethylene tetramine. Of these, the most preferable due to excellent reactivity, low cost and availability is ammonia.

The alkylene dihalide reactant may be chosen from a wide variety of difunctional organics. Preferred among these are ethylene dichloride, 1,3 - propylene dichloride and 1,2-propylene dichloride. Of these, the most preferred is ethylene dichloride.

The polymerization reaction of the above materials is preferably carried out at elevated temperatures and under superatmospheric pressures. Most preferably, to achieve the desired relatively high molecular weight polymers, the polymerization is effected at 75—200° C. under a pressure of 75—1000 psi. The reaction is accomplished by slowly introducing an amine into a reaction zone at a rate sufficient to maintain a fixed predetermined pressure within the above limits. Simultaneously, an alkylene dihalide is introduced into the reaction zone at a rate sufficient to maintain a fixed predetermined temperature within the aforementioned limits. Sufficient water should be initially introduced into the reaction zone so that reaction will occur on the liquid phase. Under these conditions polymeric polyamines having molecular weight ranging from 500 to 50,000 and more preferably 1000 to 25,000 are realized.

The following examples are given to illustrate methods by which the polymeric polyamines may be made.

Example I

A 20-gallon glass steel reactor was set up to which was attached external sources of both anhydrous gaseous ammonia and ethylene dichloride. A pressure regulator valve was inserted in the line leading from the ammonia source to the reactor. The reactor was first charged with 28 pounds of water. This was a sufficient volume to allow good agitation with the equipment employed. The reactor was heated until the temperature reached 110° C. and the system was then pressurized with anhydrous ammonia to 95—100 psi. The system was then vented to remove air, repressurized to 95—100 psi with ammonia and heated to 110° C. The pressure was maintained at the 95—100 psi level by gradual introduction of gaseous ammonia throughout the whole reaction time to replace reacted ammonia.

Ethylene dichloride was then pumped into the reactor and water cooling turned on. Initially, 15 pounds of ethylene dichloride was added over a period of one hour and fifty minutes. By introduction of the ethylene dichloride during the whole reaction the temperature of the reaction was maintained at 100—110° C. By such careful manipulation of rate of ethylene dichloride added to the system, the temperature of the exothermic reaction could be maintained relatively constant within the above recited temperature range. Upon completion of the addition of the initial 15 pounds of ethylene dichloride, an aqueous concentrate of 50% sodium hydroxide was fed into the reaction vessel in an amount of 61 pounds over three hours and 55 minutes. An additional 25 pounds of ethylene dichloride was also added during the caustic addition. Ammonia was then vented over several hours and the reaction completed by adding nine additional pounds of ethylene dichloride and sufficient sodium hydroxide to maintain the pH between about 8.5 and 11.0. At this time, the reactor had approached the capacity charge and the pumping of ethylene dichloride to the reaction zone was discontinued. The reaction was further heated for 1—2 hours to react residual ethylene dichloride. The system was then cooled and vented. The polyamide product was subjected to centrifugation and substantial amounts of sodium chloride by-product separated out from the aqueous solution of polymeric amine. Molecular weight determination of the above polyamine product demonstrated that the colecular weight was in excess of 2000 and the product contained substantially no low molecular weight polyamines such as ethylene diamine, diethylene triamine, and tetraethylene pentamine.

Example II

This example was run essentially according to the directions of Example I outlined above with the exception that ethylene dichloride (60 pounds) and calcium oxide (24 pounds) were introduced continuously along with ammonia at 100 psi into a reaction zone at a temperature of 100° C., in presence of 28 pounds of water. The reaction time was approximately five hours.

Example III

In this example 28 pounds of water was introduced into a 20-gallon glass-lined reactor and ammonia introduced at reaction temperature of 100° C., and reaction pressure of 100 psi. Five pounds of ethylene dichloride were added slowly at the above pressure and temperature and allowed to react. Following this initial ethylene dichloride addition, an additional 35 pounds was added together with 50% sodium hydroxide (70 pounds) over a period of approximately five hours. A total of 10 pounds of ammonia was employed during the total reaction time. The reactant flows were ceased, the reaction mixture stirred for thirty minutes, vented to free unreacted ammonia, and the product cooled and drummed.

Example IV

Twenty-eight pounds of water was introduced into a 20-gallon glass-line reactor along with ammonia. Reaction temperature was raised to 100° C., and pressure to 100 psi. Fifteen pounds of ethylene dichloride was also added slowly and allowed to react. Following the initial ethylene dichloride addition, another 35 pounds was added along with 70 pounds of 50% caustic solution over a period of approximately five hours. The reaction mixture after stirring for 30 minutes, vented to remove ammonia and an additional 10 pounds of ethylene dichloride added and vented one-two hours to yield the final product.

Example V

In a 20-gallon glass-lined reactor was placed the polyamine of Example IV, along with 30 pounds of sodium carbonate. The temperature was raised to 80° C. and methyl chloride admitted via a pressure regulator at 70—80 psi. In approximately seven hours, reaction was considered complete. A total of 45 pounds of methyl chloride had been added to the polyamide. The product of polyquaternary was then cooled, vented, and drummed for use.

Furthermore, U.S. Patent 3,372,129 discloses a detailed description on how to make the polymeric polyamines.

A variety of simple, inexpensive starches may be reacted with the above-described polymeric polyamines to produce a superior paper-making material upon subsequent treatment of the precursor pulp. Starches susceptible to reaction with polyamine materials are, for example, potato, corn, tapioca, and other related, readily available starches.

The starch and polymeric amine when reacted are preferably provided as a relatively dilute aqueous suspension which contains from 1 to 40% by weight of the reactants and preferably 1—30% by weight. An amount of polymeric amine is present in relation to the starch so as to provide 2—40% of polymeric amine and preferably 3—30%, in relation to and based upon the weight of the starch and polyamine.

The starch may be reacted with the polymeric polyamine either prior to, during, or subsequent to gelatinizing or cooking the starch. The aqueous suspension of starch should be treated with polyamine at a temperature ranging from 140° to 250° F. for ¼—10 hours. In the most preferred embodiment, starch in an ungelatinized state is both gelatinized and reacted with polymeric polyamines simultaneously at a temperature ranging from 185° F. to 205° F. for 1/3—5 hours. By following this variant, paper sheets of exceptionally high strengths are obtained.

As a result of reacting the starch with the polymeric polyamines the polymeric polyamine is believed to be adsorbed onto the surface of the starch.

Without limiting the invention, the following theory is offered as a possible explanation of the adsorption process:

The starch normally has a slight negative charge associated with it whereas the polymeric polyamine has a stronger positive charge. As a result the starch and polymeric polyamine are attracted via electrostatic action to one another. The resulting starch-polymeric polyamine composition has a slight positive charge since the magnitude of the positive charge of the polymeric polyamide is greater than the negative charge of the starch. The cellulosic fibers to which the starch-polymeric polyamine product is added tend to be negatively charged. As a result there is an attraction between the cellulosic fibers and the starch-polymeric polyamine composition. This attraction results in paper having improved dry strength and other improved properties.

The starch-polymeric polyamine composition product may be used in aqueous suspension form or the water may be removed by means such as vacuum filtration, to provide a dry powdery material which is easily dispersed into the wet end of the papermaking process. It has been determined that best results are realized if the starch-polymeric polyamine composition product is introduced into the paper pulp stream immediately after reaction of the starch. Generally, the starch-polymeric polyamine product should be added to the pulp at a time ranging from a few seconds after starch reaction up to about 24 hours thereafter. Most preferably the starch is incorporated into the paper stream 1—120 minutes after polyamine reaction.

The starch-polymeric polyamine composition product may be added to the pulp at a variety of areas. It is preferred that it be added after the refining step, since appreciable amounts of mechanical work effected upon the pulp deleteriously affects retention of starch to the pulp. The starch-polymeric polyamine product may be added at the refiner outlet, fan pump, consistency regulator, headbox, etc.

The process of this invention may be characterized such that the cellulosic fibers are *always* treated with a single starch-polymeric polyamine composition product. Neither the starch nor the polymeric polyamine are added separately in order or simultaneously to the cellulosic fibers.

EVALUATION OF THE INVENTION

In order to determine the efficacy of the invention, the following tests were made.

Example VI

In these series of tests, hand sheets were made involving use of both untreated starch and polymeric polyamine modified starch. The particular polymeric polyamine employed fell within the class described above, and specifically was a condensation copolymer of ammonia and ethylene dichloride. In the first test, tapioca starch was cooked and then added to pulp in an amount of 1.25% based on pulp weight. A hand sheet produced from the starch-treated pulp was then tested for burst strength and compared to a blank run involving no starch addition. In like manner, the same amount of starch was treated with the above described polymeric polyamine by addition of amine to the already cooked starch at 140° F. in varying amounts of amine based on starch weight. Burst strengths of hand sheets prepared from the pulp containing amine-modified starch were also tested. Results are listed in Table I below:

Table I

Pulp Treatment	Pulp pH	% Burst Increase Over Blank Run
Starch	5.0	7.0
11.1% Polyamine-starch	5.0	10.8
22.2% Polyamine-starch	5.0	10.2

A like series of comparative tests were run involving polyamine addition to starch slurry prior to cooking. The amine-treated starch was then cooked for 20 minutes at 201° F. and tested for efficiency in increasing sheet strength. Results are as follows:

TABLE II

Pulp Treatment	Pulp pH	% Burst Increase Over Blank Run
Starch	5.0	7.0
11.1% Polyamine-starch	5.0	10.3
22.2% Polyamine-starch	5.0	12.9

It can be readily seen from the above that the burst strengths, as measured with a mullen tester, of hand sheets containing the starch-polymeric polyamines were substantially higher than a comparative hand sheet containing only starch material.

The invention allows common starches to be utilized as papermaking additives with good results being obtained in nearly all cases. It has been observed that the best results are obtained when the starch contains at least some amylopectin in combination with amylose. It is contemplated that amylopectin alone may be used as a starch material.

Specialty starches such as dextrins, and the like, may also be utilized as a starchy material, although the invention is mainly directed toward the utilization of common non-modified starches.

Papers treated according to the invention, in addition to having improved dry strength, oftentimes will have other improved characteristics such as, for example, improved internal bond, fold, tensile and pick resistance, ply bonding, etc.

The invention also allows a smaller amount of starch to be employed and yet achieve results comparable to those obtained by excessive loadings of conventional starch treatments.

Also, it was noted that drainage properties of the wet web were improved as well as increase in machine speeds realized through use of the amine-modified starch versus sole use of starch additive.

Typical paper stocks that may be treated are kraft, bleached kraft, softwood kraft, hardwood kraft, bleached and unbleached sulfites, groundwood and alpha sulfite.

WHAT WE CLAIM IS:—

1. A starch-polymeric polyamine composition comprising 60—98% by weight of starch, and 2—40% by weight of a polymeric polyamine having a molecular weight of at least 500, said starch-polymeric polyamine having been prepared by cooking an aqueous suspension of said starch with said polymeric polyamine at a temperature of 140—250° F. for $\frac{1}{4}$—10 hours, said polyamine being formed by reaction of an alkylene dihalide and an amine having the following structural formula:

$$H_2N(-R-\overset{\displaystyle H}{\overset{|}{N}}-)_xH$$

where R is an alkylene radical selected from

$$-CH_2CH_2-,\ -CH_2CH_2CH_2-,\ \text{and}$$

$$-CH_2-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-,$$

and x is an integer of 0—5.

2. The starch-polymeric polyamine composition of claim 1 wherein said polymeric polyamine is an ammonia-ethylene dichloride condensation polymer having a molecular weight of at least 1000.

3. A process for the production of paper having improved strength and other improved properties which comprises the sequential steps of forming an aqueous cellulosic fiber suspension, adding to said suspension as a single product at a point prior to its formation into a sheet, a polymeric polyamine starch composition, said starch composition having been prepared by reacting a 60—98% by weight aqueous suspension of starch with 2—40% by weight of a polymeric polyamine having a molecular weight of at least 500 at a temperature of 140—250° F. for $\frac{1}{4}$—10 hours, said polyamine being formed by reaction of an alkylene dihalide and an amine having the following structural formula:

$$H_2N(-R-\overset{\displaystyle H}{\overset{|}{N}})_xH$$

where R is an alkylene radical selected from

$$-CH_2CH_2-,\ -CH_2CH_2CH_2-, \text{ and}$$

$$-CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-,$$

and x is an integer of 0—5; and then forming said aqueous cellulosic fiber suspension containing said polymeric polyamine starch into a sheet.

4. The process of claim 3 wherein said polymeric polyamine has a molecular weight of at least 1000.

5. The process of claim 2 or 3 where said polyamine polymer is an ammonia-ethylene dichloride condensation polymer.

6. A starch-polymeric polyamine composition according to claim 1, substantially as herein described.

7. A process for the production of paper according to claim 3 substantially as herein described.

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